Spectrophotometric Determination of Hydrazine with Para-(Dimethylamino) Benzaldehyde in Aqueous Streams of Purex Process

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***Abstract*-In the present work, the direct, sensitive, and accurate method for the determination of hydrazine is described. The method is based on the formation of yellow coloured azine complex by hydrazine with *para*-(dimethylamino)benzaldehyde (p-DMAB) in 1*M* nitric acid medium. The formed yellow coloured azine complex is stable in acidic medium and has a maximum absorbance at 454 *nm*. The working range of acidity should be within 0.1 to 1.0 *M* nitric acid medium. A calibration graph was made for the concentration range of hydrazine from 0.0145 to 0.125 $\mu g/mL$. The molar absorption coefficient at 454 nm, detection limit and Sendell's sensitivity are 6.06×10^4 $L.mol^{-1}.cm^{-1}$, 0.0132 $\mu g/mL$ and 8.25×10^{-6} $\mu g/cm^{-2}$ respectively. Relative standard deviation was less than 2% and correlation coefficient was 0.999. The proposed method was applied directly to the determination of hydrazine in purex process and it is applicable for the analysis of polluted river water / boiler water/water streams of nuclear reactors.**

Keywords-Hydrazine; Para - (dimethylamino) benzaldehyde; Spectrophotometer; Nitric Acid; Purex Process

I. INTRODUCTION

Hydrazine and its derivatives are used in many industries, agriculture, and other fields including the manufacture of metal films, photographic chemicals, dyes, explosives, insecticides and blowing agents for plastics. Its important uses are as a high-energy rocket propellant, as a reactant in military fuel cells, in nickel plating, in the polymerization of urethane, for removal of halogens from waste water, as an oxygen scavenger in boiler feed water to inhibit corrosion and in photographic development [1]. Hydrazine is also used as a scavenger of nitrous acid in the Purex process for the separation of uranium and plutonium from each other [2] and for the solvent cleanup process [3]. An application is the use of hydrazine nitrate-HNO_3-KF solutions for dissolving plutonium metal [4]. On the other hand, hydrazine is highly toxic and irritant and has been recognized as a carcinogenic, mutagenic, and hepatotoxic substance. Therefore, its detection has attracted considerable analytical interest. Various methods are described in the literature for the determination of hydrazine, using different analytical techniques, such as spectrophotometry [5-7], spectrofluorimetry [8-9], voltametry [10-11], amperometry [12], coulometry [13], titrimetry [14], gas chromatography [15], ion selective electrode [16], Potentiometry [17] and indirect methods [18]. However, most of the existing methods either lack sufficient sensitivity [15] or require complicated and expensive instruments. With the aim of optimizing hydrazine concentration in the process, an on-line measurement is required which is not yet available. Optical fiber probes are chosen because they represent a new technology for on-line measurements. Therefore, the need for a sensitive, simple, and reliable method for the determination of hydrazine is realized. In the present paper, the direct, simple, sensitive and precise spectrophotometric method based on reducing properties of hydrazine with *para*-(dimethylamino) benzaldehyde is described and this method is applied in the determination of hydrazine in the presence of uranium in aqueous stream of nuclear fuel reprocessing. This method also suitable for on-line monitoring of hydrazine is possible with fiber optical probes/chemical sensors.

II. EXPERIMENTAL

A. Instrumentation

An indigenously developed fiber optic aided spectrophotometer, using a 4 cm path length fiber optic probe is used for absorbance measurements.

B. Reagents

Doubly distilled water and analytical reagent grade chemicals were used for solution preparation. 0.4 M Hydrazine nitrate (AR-Orion Chem.Pvt.Ltd, Mumbai) was prepared. From this standard solution of hydrazine was made with suitable aliquot. The hydrazine solutions were standardized by titrimetry [19-21]. 4.4751 g of (AR-Prolabo, purity 98%) para-(dimethylamino) benzaldehyde was dissolved in 1M HNO_3 and made up to the mark, with double distilled water. Nuclear grade U_3O_8 was dissolved in 1:1 nitric acid and uranium concentration was determined by potentiometric redox titration using Davies and Gray method [22]. 1M nitric acid (AR-Fischer, assay of 69-71%) was prepared with distilled water.

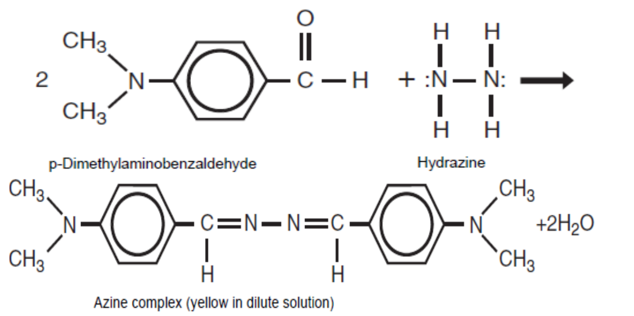
C. Procedure

A stock hydrazine solution was prepared in distilled water and from this stock solution various hydrazine standards were prepared. Each of a series of 10 mL volumetric standard flask was added 0.1 mL of para-(dimethylamino) benzaldehyde and suitable aliquot of solution of hydrazine. Solution of 1M nitric acid was added to make up the volume. A period of 15 mins was allowed to obtain full colour development. The absorbance of the (para-(dimethylamino) benzalazine) yellow coloured dye was measured at 454 nm. A reagent blank was prepared in the same manner. The reaction between hydrazine and p-DMAB in 1M nitric acid was studied with fiber optic aided spectrophotometry by monitoring the absorbance at frequent intervals over the range of 550-380 nm.

III. RESULTS AND DISCUSSION

The condensation reactions of aromatic aldehydes with hydrazine and its derivatives produce coloured products. The

condensation reaction involves a complex formation of hydrazine with p-DMAB to form *para*-(dimethylamino) benzalazine [23] called yellow coloured azine complex according to the stoichiometric equation which is shown in Illustration.1. This reaction is well known in organic chemistry to protect carbonyl group [24]. Reaction is reversible by a change of acidity to recover carbonyl group. Hydrazine has no absorbance band in the ultra-violet and visible range. But it combines with *para*-(dimethylamino) benzaldehyde to form a yellow coloured complex which is stable in acidic medium and has maximum absorption at 454 nm measured using fiber optic aided spectrophotometry. The absorbance was plotted against the concentration of hydrazine in Fig. 1, which shows the typical calibration graph for hydrazine at 454 nm in 1*M* nitric acid medium with RSD 1% and correlation coefficient of 0.999. This calibration graph showed good agreement with Beer's law over the concentration range investigated that was 0.0145 to 0.125 *µg/mL*. It was observed that, the reaction of hydrazine with p-DMAB was very fast and completely by 5 min in acidic medium at room temperature. No measurable absorbance change is observed in different concentration of hydrazine with *p*-DMAB in 24 hours. The unknown concentration of hydrazine in the sample was determined by using standard calibration graph. A typical absorption spectral characteristic of yellow coloured azine complex at 454 nm in 1*M* nitric acid medium is shown in Fig. 2. To determine the molar extinction, coefficient of azine complex was found to be 6.06×10^4 $L.mol^{-1}.cm^{-1}$ computed as in Table. 1. The high value of molar absorptivity (ε) allows a better sensitivity and a low limit of detection. The detection limit and Sandell's sensitivity were found 0.0132 *µg/mL* and 8.25×10^{-6} $\mu g/cm^{-2}$ respectively.



$2(CH_3)_2N{-}C_6H_5{-}CHO + NH_2NH_2 \rightleftharpoons (CH_3)_2N{-}C_6H_5{-}HC{=}N{-}N{=}CH{-}H_5C_6{-}N(CH_3)_2 + H_2O$

Illustration.1

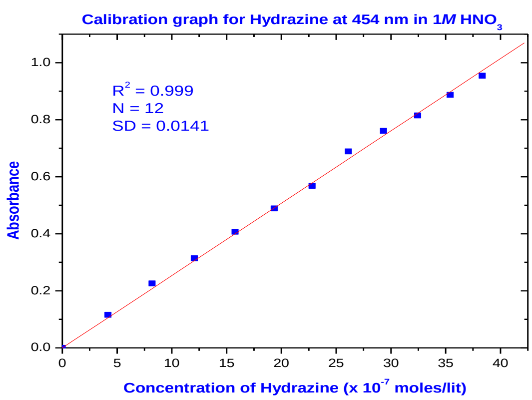


Fig. 1 Calibration graph for Hydrazine at 454 nm with p-(dimethylamino)benzaldehyde in 1M HNO3

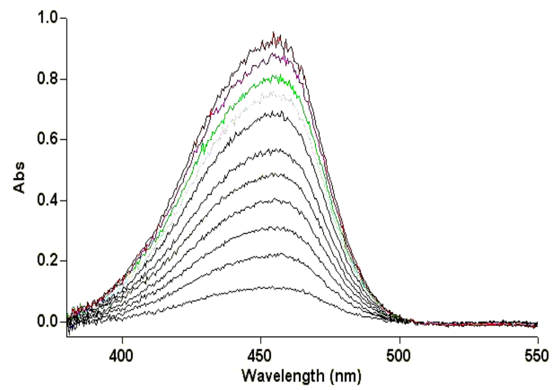


Fig. 2 Typical absorption spectrum of hydrazine with p-(dimethylamino)benzaldehyde

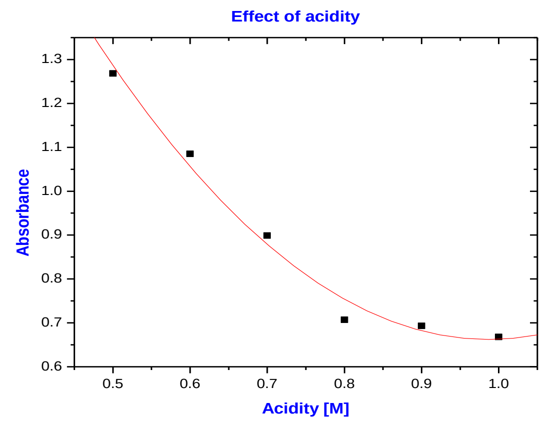


Fig. 3 Graphical format of hydrazine with pDMAB in various acid concentrations from 0.5 *M* to 1.0*M* HNO_3

TABLE I
DETERMINATION OF MOLAR ABSORPTIVITIES OF HYDRAZINE WITH P-DMAB AT 454 NM IN 1M NITRIC ACID MEDIUM

Conc.N_2H_4 (ppm)	Absorbance	Molar Absorptivities ($L.mol^{-1}cm^{-1}$)
0.015	0.116	64155.74
0.029	0.226	61833.11
0.042	0.314	61171.62
0.054	0.407	60791.63
0.646	0.489	60580.53
0.075	0.568	60435.17
0.092	0.695	60272.31
0.100	0.759	60209.42
0.108	0.815	60165.36
0.118	0.887	60113.18
0.127	0.954	60071.78
Average		60564.41

TABLE II
EFFECT OF NITRIC ACID IN HYDRAZINE WITH PDMAB

Acid concentration (M)	Absorbance
0.5	1.268
0.6	1.085
0.7	0.899
0.8	0.707
0.9	0.693
1.0	0.668

A. Effect of Nitric Acid Concentrations

In the range of acidity from 0.5 to 1*M* HNO_3, the absorbance of hydrazine-p-DMAB dye complex gradually decreases. Above the acidity of 2*M* HNO_3, no yellow coloured dye was formed. The equilibrium is fully shifted to the left or *para*-(dimethylamino)benzalazine is decomposed by high acidity. From 0.1 to 0.4 *M* nitric acid, a strong yellow colour product appeared at 454 nm. Fig. 3 shows that from 0.5 to 1.0 *M* nitric acid medium graphically represents that absorbance decreases. From this study, both phenomena may be explained. In lower acidity, from 0.1 to 2*M*, the structure of p-DMAB is not fundamentally modified. Probably, the variation of absorbance may be due to the protonation of the amino group, which is equilibrium. In higher acidity, the structure of the p-DMAB may be reversibly modified. Table 2 provides the data of the no change in absorbance from 0.8-1.0*M* nitric acid. From this table, it is obvious that in this range of (0.8-1.0 M) nitric acid is only used in purex process of partitioning step using uranous nitrate solutions.

B. Effect of Para-(dimethylamino)Benzaldehyde

In pushing the yellow colour azine complex-forming (p-(dimethylamino)benzalaine) reaction to completion with increasing the concentration of p-DMAB. Reproducibility in the spectrophotometric analysis requires that the equilibrium be shifted as fully as possible toward the p-(dimethylamino) benzaline. At the same time, p-DMAB is itself moderately absorbing, so that its concentration should be minimized to reduce the background absorbance of the sample solutions. Very small volume of para-(dimethylamino) benzaldehyde **i.e**. 0.1 mL is sufficient for making the yellow dye complex. Effect of p-DMAB concentration is presented in the graphical form shown in Fig. 4. It gives the gradual increase of the absorbance with the increase of the concentration/volume of p-DMAB added to develop the yellow dye complex of hydrazine with complexing agent.

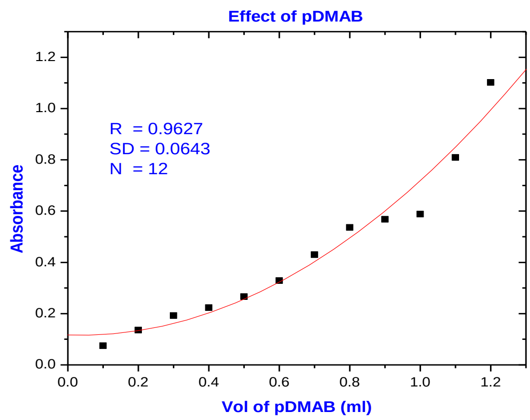


Fig. 4 Effect of p-(dimethylamino)benzaldehyde in determination of hydrazine

C. Effect of U(IV) Nitrate

To assess the validity of the method, hydrazine was determined in the presence of known amounts of those species which are commonly found with uranous nitrate solution. Uranous nitrate doesn't interfere in this method. Fig. 5 shows that no effect of uranous nitrate in hydrazine analysis with para-(dimethylamino) benzaldehyde. Table 3 shows that no interference of uranous nitrate ions in real samples contained hydrazine. It indicates no change in absorbance with the increase of U (IV) concentrations.

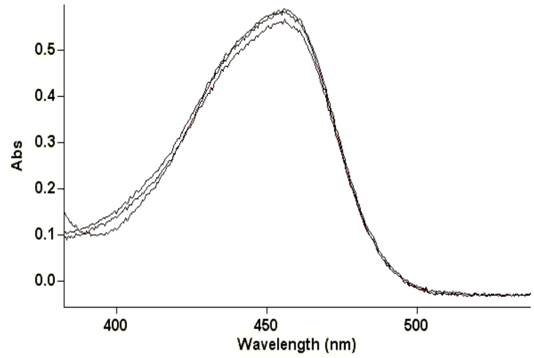


Fig. 5 Effect of U (IV) nitrate solution: Typical absorption spectrum of hydrazine with pDMAB in presence of uranous nitrate solution

TABLE III
EFFECT OF URANOUS NITRATE IN HYDRAZINE DETERMINATION

U(IV) Concentration, (g/L)	Absorbance
0.775	0.568
3.755	0.588
7.55	0.584

TABLE IV
COMPARSION OF RESULTS WITH TWO DIFFERENT ANALYTICAL TECHNIQUES

Concentration of hydrazine (ppm)	
Present method	Modified spectrophotometric methods [25-26]
8.196	8.288
1.072	1.040
2.30	2.80
4.419	4.512

D. Analytical Application

The efficiency of the developed technique for the spectrophotometric determination of hydrazine in real samples was established by comparing the results with those obtained with hydrazine determination in the presence of uranium by modified spectrophotometric methods [25-26]. The results are represented in Table. 4 and are found to be in good agreement. Fig. 6 refers the chromatogram of hydrazine in the presence of uranium and nitrate ion. Higher concentration of hydrazine can be determined by diluting the sample.

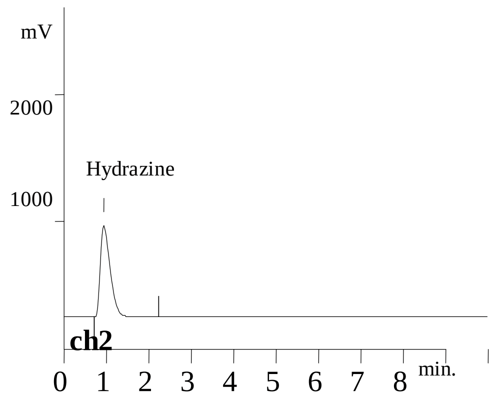


Fig. 6 Typical real sample chromatogram of Hydrazine (25 ppm) in presence of uranium using modified spectrophotometry [26]

IV. CONCLUSION

The developed spectrophotometric method, based on condensation reaction hydrazine with *para*-(dimethylamino) benzaldehyde, is simple, sensitive and applicable to all range of uranium and hydrazine concentration relevant to purex process used for nuclear fuel reprocessing. Results obtained by the developed procedure for hydrazine in samples were compared with those obtained from modified spectrophotometric [25-26] methods. The results are found to be in good agreement. The proposed method offers good selectivity, accuracy, and precision and can be applied for a very low range of hydrazine concentration. It is simpler than other methods.

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